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## DESCRIPTION

### SEMICONDUCTOR-FERROELECTRIC STORAGE DEVICES AND PROCESSES FOR PRODUCING THE SAME

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#### Technical Field

The present invention relates to semiconductor-ferroelectric storage devices and processes for producing the same. More particularly, the present invention relates to semiconductor-ferroelectric storage devices employing as a memory cell a transistor comprising a ferroelectric film in a gate insulation film, and processes for producing the devices.

#### 15 Background Art

Transistors employing a ferroelectric as a gate insulation film are expected to be next-generation highly integrated memories because data storage, data readout, and writing are conducted in the individual transistors. In this kind of transistor, electrical conduction in the transistor is controlled according to the direction of electric polarization of the ferroelectric. Virtually, structures comprising an insulator buffer layer inserted between a semiconductor and a ferroelectric so as not to impair the features of both of the semiconductor and the ferroelectric have been investigated (see, for example,

patent documents 1 and 2). Transistors of this structure including the metal gate electrode in contact with the ferroelectric are called MFIS (Metal-Ferroelectrics-Insulator-Semiconductor) transistors.

5           In principle, the MFIS transistors are expected to have the following features: (1) no data disappear even when the power is turned off, because electric polarization is utilized; (2) the only thing necessary for a readout operation is to check the electrical conduction between the  
10   source and the drain in the transistor, and the contents of the data remain undestroyed even after the readout operation; and (3) the speed of data readout and writing are as high as that of DRAMs.

          However, the MFIS transistors heretofore have had a  
15   problem that after data writing, the data disappear in terms of memory transistor operation in about 1 day at most (see, for example, non-patent documents 1 and 2).

Patent Document 1 : JP-A-2001-291841

Patent Document 2 : JP-A-2002-353420

20   Non-Patent Document 1 : S. Migita et al., *Integrated Ferroelectrics*, Vol.40, pp.135-143, 2001

Non-Patent Document 2 : Shinji Migita et al., *Denshi Jôhô Tsûshin Gakkai Ronbun-shi*, Vol.J85-C, No.1 (January 2002 issue), pp.14-22

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## Disclosure of the Invention

As described above, the MFIS transistors heretofore have failed to hold data over a period which enables practical use. This is mainly because the buffer layer and the ferroelectric have a high leakage current and, hence, charge is accumulated around the interface between the ferroelectric and the buffer layer, and this charge shields the electric polarization in the ferroelectric, making it impossible for the electric polarization of the ferroelectric to control electrical conduction between the source and drain in the transistor.

Furthermore, there is a problem that although a voltage is applied to the MFIS in data writing in the ferroelectric, most of the voltage acts on the buffer layer when the buffer layer has a low dielectric constant.

The problems of the related-art described above are to be solved by the present invention. An object thereof is to provide an MFIS type memory device capable of holding data over a period which enables practical use.

In order to accomplish the object described above, the present invention provides a semiconductor-ferroelectric storage device, which comprises a transistor comprising a semiconductor substrate or semiconductor region having a source region and a drain region and, on which an insulator buffer layer, a ferroelectric film, and a gate electrode are layered in this order, wherein the

insulator buffer layer is an insulating film comprising a hafnium-aluminum oxide as a main component.

Preferably,  $x$  indicating the constitution ratio,  $\text{Hf}_{1-x}:\text{Al}_{2x}$ , between said hafnium element and said aluminum  
5 element in the insulator buffer layer is within a ratio of  $0 < x < 0.7$ .

More preferably, the insulator buffer layer contains a nitrogen element as an additive.

In order to accomplish the object, the present  
10 invention further provides a semiconductor-ferroelectric storage device, which comprises a transistor comprising a semiconductor substrate or semiconductor region having a source region and a drain region and, on which an insulator buffer layer, a ferroelectric film, and a gate electrode  
15 are layered in this order, wherein the insulator buffer layer is an insulating film comprising a hafnium oxide as a main component and contains a nitrogen element as an additive.

Preferably, the nitrogen element is contained in an  
20 amount of from  $1 \times 10^{19} \text{ cm}^{-3}$  to  $1 \times 10^{22} \text{ cm}^{-3}$ .

More preferably, an oxide film, a nitride film, or an oxynitride film is inserted between the semiconductor substrate and the insulator buffer layer.

In order to accomplish the object, the present  
25 invention furthermore provides a process for producing a semiconductor-ferroelectric storage device, which comprises

a transistor comprising a semiconductor substrate or semiconductor region having a source region and a drain region and, on which an insulator buffer layer comprising a hafnium-aluminum oxide as the main component, a

5 ferroelectric film, and a gate electrode are layered in this order, said process comprising a treatment of a semiconductor surface, a formation of the insulator buffer layer, a formation of the ferroelectric film, a formation of the gate electrode, and a heat treatment.

10 Preferably, the formation of the insulator buffer layer is conducted in an atmosphere comprising nitrogen gas.

In order to accomplish the object, the invention still further provides a process for producing a  
15 semiconductor-ferroelectric storage device, which comprises a transistor comprising a semiconductor substrate or semiconductor region having a source region and a drain region and, on which an insulator buffer layer comprising a hafnium oxide as a main component, a ferroelectric film,  
20 and a gate electrode are layered in this order, said process comprising a treatment of a semiconductor surface, a formation of the insulator buffer layer, a formation of the ferroelectric film, a formation of the gate electrode, and a heat treatment, wherein the formation of the  
25 insulator buffer layer being conducted in an atmosphere comprising nitrogen gas.

Preferably, the atmosphere comprising nitrogen gas is a mixed-gas atmosphere comprising nitrogen and oxygen in a molar ratio of from 1:1 to  $1:10^{-7}$ .

More preferably, a heat treatment is conducted at  
5 least one time in any timing and environment selected from:  
in a vacuum vessel for ferroelectric-film formation during  
the formation of the ferroelectric film; in a vacuum vessel  
for ferroelectric-film formation after the formation of the  
ferroelectric film; in an annealing furnace after the  
10 formation of the ferroelectric film and before the  
formation of the gate electrode; and in an annealing  
furnace after the formation of the gate electrode.

According to the present invention, data writing  
and readout can be realized in a one-transistor size, and  
15 the data which has been written never disappear over a  
practically sufficient prolonged period of time. In  
addition, the contents of the data remain undestroyed even  
after readout. The devices according to the present  
invention can be used in a variety of circuits, not only as  
20 semiconductor memories for a wide range of applications but  
also as stable temporary storage devices in semiconductor  
logic circuits.

#### Brief Description of the Drawings

25 Fig. 1 is an overview illustrating a transistor  
according to the present invention.

Fig. 2 is a drawing showing the relationship between gate voltage and drain current in Example 1.

Fig. 3 is a drawing showing changes of drain current with time in the transistor according to Example 1.

5 Fig. 4 is a drawing showing the relationship between gate voltage and drain current in Example 2.

Fig. 5 is a drawing showing changes of drain current with time in the transistor according to Example 2.

Fig. 6 is a drawing showing the relationship  
10 between sweep gate voltage and memory window width in Example 1.

Fig. 7 is a drawing showing the relationship between gate voltage and gate leakage current in Example 1.

Fig. 8 is a drawing showing the relationship  
15 between the number of rewriting operations and drain current in Example 1.

Fig. 9 is a drawing showing the relationship between gate voltage pulse width and drain current in Example 1.

20 Fig. 10 is a drawing showing the relationship between gate voltage and gate leakage current in Example 2.

Fig. 11 is a drawing showing the relationship between the composition  $x$  in  $\text{Hf}_{1-x}\text{Al}_{2x}\text{O}_{2+x+y}$  and memory window width in Examples 1 to 7.

25 Fig. 12 is a drawing showing changes of drain current with time in the transistor according to Example 5.

Fig. 13 is a drawing showing the relationship between the molar proportion of oxygen (to nitrogen) and memory window width in Examples 1 and 8.

Fig. 14 is a drawing showing changes of drain  
5 current with time in the transistor according to Example 9.

Fig. 15 is a drawing showing changes of drain current with time in the transistor according to Example 10.

#### 10 Best Mode for Carrying Out the Invention

Fig. 1 is an overview of a semiconductor-ferroelectric storage device according to the present invention. For producing the device according to the present invention, a semiconductor substrate 1 is prepared  
15 first. This semiconductor substrate 1 may be silicon, germanium or silicon/germanium mixed crystal or may be SiC or GaAs, and the kind thereof is not limited. It is also possible to use an SOI (silicon on insulator) substrate in place of the semiconductor substrate.

20 One side 2a of an insulator buffer layer 2 is connected to one side of the semiconductor substrate 1. As the insulator buffer layer 2 is formed an oxide  $\text{HfO}_{2+u}$ , which contains hafnium as a constituent element, or an oxide  $\text{Hf}_{1-x}\text{Al}_{2x}\text{O}_{2+x+y}$ , which contains hafnium and aluminum as  
25 constituent elements. It is especially preferable that the range of  $x$  is  $0 < x < 0.7$  from the standpoints of enhancing



thermal stability and chemical stability and of having a high dielectric constant. It is especially preferable that the range of  $y$  is  $-0.2 < y < 0.2$  from the standpoint of showing good insulating properties. It is also especially preferable that the range of  $u$  is  $-0.2 < u < 0.2$  from the standpoint of showing good insulating properties. It is especially preferable that the thickness  $t$  of each of the  $\text{HfO}_{2+u}$  and  $\text{Hf}_{1-x}\text{Al}_{2x}\text{O}_{2+x+y}$  is in the range of  $4 \text{ nm} < t < 40 \text{ nm}$  from the standpoint of reducing the absolute value of the applied voltage for data writing, i.e., for determining the state of electric polarization.

One side 3a of a ferroelectric film 3 is connected to the other side 2b of the insulator buffer layer 2. Although the kind of the ferroelectric is not limited, typical examples thereof include  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ,  $\text{SrBi}_2(\text{Ta}_{1-z}\text{Nb}_z)_2\text{O}_9$ ,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ,  $\text{Bi}_{4-2}\text{La}_2\text{Ti}_3\text{O}_{12}$ ,  $\text{PbZr}_{1-z}\text{Ti}_z\text{O}_3$ , and  $\text{YMnO}_3$ . It is especially preferable that the thickness  $d$  of the ferroelectric film is in the range of  $20 \text{ nm} < d < 600 \text{ nm}$  from the standpoint of reducing the absolute value of the applied voltage for data writing, i.e., for determining the state of electric polarization.

A gate electrode 4 is connected to the other side 3b of the ferroelectric film 3. The gate electrode 4 may be any material having good electrical conductivity. For example, it may be a metal such as gold or platinum, a nitride such as  $\text{TiN}$  or  $\text{TaN}$ , or an oxide such as  $\text{IrO}_2$  or

RuO<sub>2</sub>. Furthermore, the gate electrode 4 may be a multilayered film such as Pt/TiN/Ti or IrO<sub>2</sub>/Ir.

The semiconductor substrate 1 has a source region 5 and a drain region 6. In the case where the source region 5 and the drain region 6 are n-type, the region 7 other than the source region 5 and drain region 6 is p-type. In the case where the source region 5 and drain region 6 in the semiconductor substrate 1 are n-type, the region 7 other than the source region 5 and drain region 6 is p-type.

#### Effects

Data storage is based on the electric polarization of the ferroelectric film 3. In order to have ferroelectricity, the ferroelectric film 3 should be heated to a high temperature, during the thin-film formation or in a subsequent heat treatment, to thereby bring the film 3 into a crystalline state. This crystallization temperature is generally from 650°C to 950°C. In general, the higher the temperature, the better the crystallinity and ferroelectricity. The period of the crystallization step is typically 1 hour. For forming a source region and a drain region in the silicon, a short-time (typically 30 seconds) heat treatment at a temperature of at least about 1050°C is necessary for activation of the impurities. The insulator buffer layer 2 inevitably undergoes this high-

temperature step for crystallizing the ferroelectric film

3. In a standard production process, the buffer layer 2

further undergoes a heat treatment step for forming a

source region and a drain region. Accordingly, in

5 processes heretofore, the insulator buffer layer 2 is also

disadvantageously crystallized in the heat treatment step

and this has resulted in leakage current flowing through

grain boundaries between crystal grains. In the case of

the  $\text{HfO}_{2+u}$  or  $\text{Hf}_{1-x}\text{Al}_{2x}\text{O}_{2+x+y}$  in this embodiment, the insulator

10 buffer layer 2 is not crystallized but retains the

amorphous state even in the thermal step for ferroelectric

crystallization or in the thermal step for activation of

the impurities. Consequently, the insulator buffer layer 2

can have a reduced leakage current. The surface of the

15 insulator buffer layer 2 in an amorphous state is smoother

than the insulator buffer layer which has been

crystallized. Seed crystals for the growth of crystals of

a ferroelectric film 3 are less apt to generate from the

surface of the amorphous insulator buffer layer 2.

20 Accordingly, crystal grains of ferroelectric film 3 can be

small, dense thin film can be formed, and the leakage

current flowing through the ferroelectric film 3 can be

reduced. On the other hand, when the insulator buffer

layer 2 is crystallized, this layer has enhanced surface

25 irregularities due to the crystal grains and grain

boundaries. These crystal grains are apt to generate seed

crystals for a ferroelectric film 3, and the resultant ferroelectric film 3 is constituted of large crystal grains and has an increased leakage current. As described above, by constituting an insulator buffer layer 2 of  $\text{HfO}_{2+u}$  or  $\text{Hf}_{1-x}\text{Al}_x\text{O}_{2+x+y}$ , the leakage current flowing through each of the insulator buffer layer 2 and the ferroelectric film 3 can be reduced and a memory transistor having a truly sufficient long data holding time is realized.  $\text{Hf}_{1-x}\text{Al}_x\text{O}_{2+x+y}$  retains its amorphous state at even higher temperatures than  $\text{HfO}_{2+u}$  in a heat treatment step and, hence, is especially preferred when a ferroelectric having a high crystallization temperature is used as the ferroelectric film 3.

## 15 Production Processes

Production processes are explained next. It is a matter of course that the production processes of the present invention should not be construed as being limited to the following processes.

20 For forming the insulator buffer layer 2, any technique for thin-film formation can be used. Effective techniques for physical vapor deposition include pulsed-laser deposition (also called laser ablation), sputtering, and vapor deposition. Examples of chemical deposition include MOCVD (metal organic chemical vapor deposition), 25 MOD (metal organic decomposition), and a sol-gel method.

For forming the ferroelectric film 3 and the gate electrode 4 also, any technique for thin-film formation can be used. Effective techniques for physical vapor deposition include pulsed-laser deposition, sputtering, and  
5 vapor deposition. Examples of chemical deposition include MOCVD, MOD, and a sol-gel method.

An example of production processes is explained below in which silicon is used as a semiconductor substrate 1 and pulsed-laser deposition is used for forming an  
10 insulator buffer layer 2 and a ferroelectric film 3.

#### 1. Treatment of Silicon Surface

A silicon surface is cleaned by a standard surface-cleaning method. Thereafter, the oxide layer remaining on  
15 the surface is removed with dilute hydrofluoric acid or buffered hydrofluoric acid. Furthermore, a surface treatment for, e.g., purposely forming an oxide film, nitride film, or oxynitride film composed of from one to several molecular layers may be conducted.

20

#### 2. Formation of Insulator Buffer Layer 2

The layer is formed by pulsed-laser deposition. For the purpose of inhibiting the formation of an oxide layer having a low permittivity, such as  $\text{SiO}_2$ , the temperature of  
25 the silicon during layer formation is kept low (from room temperature to  $550^\circ\text{C}$ ). When the insulator buffer layer 2

is an oxide containing hafnium and aluminum as constituent elements, a target composition of  $\text{Hf}_{1-x}\text{Al}_{2x}\text{O}_{2+x+y}$  is used. Alternatively,  $\text{HfO}_{2+u}$  and  $\text{Al}_2\text{O}_3$  may be used. In this case, although the two targets may be simultaneously vaporized (sputtered), use may be made of a method in which the two targets are each alternately vaporized one or more times to synthesize  $\text{Hf}_{1-x}\text{Al}_{2x}\text{O}_{2+x+y}$  through a heat treatment. When  $\text{HfO}_{2+u}$  and  $\text{Al}_2\text{O}_3$  are alternately deposited, it is especially preferred to deposit  $\text{HfO}_{2+u}$  first. When the insulator

buffer layer 2 is an oxide containing hafnium as a constituent element, a target composition of  $\text{HfO}_{2+u}$  is used.

Since the insulator buffer layer 2 is an oxide, oxygen gas is introduced during formation. It is especially preferred to mix oxygen gas with nitrogen gas for the purpose of inhibiting and diminishing the formation of an oxide layer having a low-permittivity at the interface between the silicon and the insulator buffer layer 2. Nitrogen can also diminish structural defects in the insulator buffer layer 2 and reduce leakage current. When an

oxygen/nitrogen mixed gas is used, the N:O mixing molar ratio is from 1:1 to  $1:10^{-7}$ . Furthermore, since the  $\text{Hf}_{1-x}\text{Al}_{2x}\text{O}_{2+x+y}$  and  $\text{HfO}_{2+u}$  targets themselves contain oxygen and because hafnium atoms and aluminum atoms readily form oxides, nitrogen gas only may be introduced during the formation of an insulator buffer layer 2. In this case, the mixing molar ratio is determined by the amount of

residual oxygen contained in the nitrogen gas. Although the mixing molar ratio between nitrogen and residual oxygen, N:O, is typically from  $1:10^{-5}$  to  $1:10^{-7}$ , the molar ratio of oxygen gas to nitrogen gas may be smaller than  
5 that.

As a result of the film formation in an atmosphere comprising nitrogen gas, a nitrogen element is added as an additive to the insulator buffer layer. Thus the effects described above can be provided. The content of the  
10 nitrogen element is preferably in a range of from  $1 \times 10^{19}$   $\text{cm}^{-3}$  to  $1 \times 10^{22}$   $\text{cm}^{-3}$ . It is especially preferable that the range thereof is from  $5 \times 10^{19}$   $\text{cm}^{-3}$  to  $5 \times 10^{21}$   $\text{cm}^{-3}$ .

### 3. Formation of Ferroelectric Film 3

15 The film is formed by pulsed-laser deposition. Use may be made of a method in which silicon as a semiconductor substrate 1 is placed in the same vacuum vessel for thin-film formation as in the formation of the insulator layer 2 described above, and an insulator buffer layer 2 and a  
20 ferroelectric film 3 are successively formed by pulsed-laser deposition without taking the silicon out of the vessel. This method is especially preferred because the interface between the insulator buffer layer 2 and the ferroelectric film 3 is kept clean and excellent electrical  
25 properties are obtained. During the formation of the ferroelectric film 3, oxygen gas is introduced.

#### 4. Formation of Gate Electrode

In the case of platinum, for example, a platinum gate electrode is formed by vapor deposition with electron beam heating, by sputtering or pulsed-laser deposition.

5

#### 5. Heat Treatment Step

A heat treatment is conducted for crystallizing the ferroelectric film 3. There are the following four cases of heat treatment timing, and at least one of these cases is carried out.

(1) Heat treatment during the thin-film formation in step 3 described above. (2) Heat treatment in the vacuum vessel for thin-film formation after the thin-film formation in step 3 described above. (3) Heat treatment in an annealing furnace after the thin-film formation in step 3 and before step 4. (4) Heat treatment in an annealing furnace after step 4.

When the ferroelectric film 3 is  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ , the heat treatment temperature for crystallization is from 650°C to 900°C.

In this heat treatment step for crystallization, when an oxygen is supplied to the surface of the silicon substrate, there are cases where a silicon oxide film may grow at the interface between the substrate and the insulator buffer layer or at the interface between the substrate and a surface treatment film, e.g., an oxide



film. According to the invention, since a nitrogen element is added to the insulator buffer layer, oxygen movement is inhibited and, hence, the growth of a silicon oxide film is inhibited. Simultaneously, it is expected that the  
5 ferroelectric film is inhibited from being reduced by the heat treatment.

[Example 1]

The materials used and the thicknesses thereof are  
10 as follows.

Semiconductor substrate 1: Si

Insulator buffer layer 2:  $\text{Hf}_{1-x}\text{Al}_{2x}\text{O}_{2+x+y}$ ;  $x=0.25$ ;  $y=0$ ;  
thickness of 10 nm

Ferroelectric film 3:  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ; thickness of 400  
15 nm

Gate electrode 4: Pt; thickness of 200 nm; gate  
length (length of distance from source region to drain  
region) of 10  $\mu\text{m}$

Conductivity type of source region 5 and drain  
20 region 6: n-type

Conductivity type of region 7: p-type

$\text{Hf}_{1-x}\text{Al}_{2x}\text{O}_{2+x+y}$  ( $x=0.25$ ;  $y=0$ ) as an insulator buffer  
layer 2 was formed by pulsed-laser deposition. The laser  
used was a KrF excimer laser. The laser energy was 250 mJ  
25 per pulse, the pulse repetition frequency was 2 Hz, and the  
deposition time was 270 seconds. The temperature of the

substrate was 200°C. The introduction gas was a nitrogen/oxygen mixed gas, in which the molar ratio N:O was 1:10<sup>-6</sup>. The pressure of this introduction gas in the deposition chamber was 0.1 Torr (13.33 Pa). SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>

5 corresponding to a ferroelectric film 3 was also formed by pulsed-laser deposition. The kind and energy of the laser were the same as in the case of the insulator buffer layer 2 described above. The pulse repetition frequency was 5 Hz and the deposition time was 34 minutes. The temperature of

10 the substrate was 400°C. The introduction gas was oxygen. The pressure of this introduction gas in the deposition chamber was 0.1 Torr (13.33 Pa). Platinum was formed as a gate electrode 4 by electron-beam vacuum deposition. After the formation of the gate electrode, a heat treatment was  
15 conducted at 800°C in oxygen at atmospheric pressure for 1 hour in order to crystallize the SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>. A transistor was produced by using techniques for use in semiconductor device production steps, such as photolithography and ion beam etching.

20 Properties of the transistor produced in Example 1 above are then shown. Fig. 2 shows the results of a drain current I<sub>D</sub> when a gate voltage V<sub>G</sub> was applied to the gate electrode 4. The gate voltage was continuously changed from 6 V to -6 V and then changed from -6 V to 6 V. The  
25 drain current changed as shown in Fig. 2 according to the specific properties of the ferroelectric. With the sweep

of gate voltage, the drain current changed as shown by the arrows. The transistor can come into either of two states, i.e., an ON state and an OFF state, according to the direction of electric polarization memorized as represented by the two points shown in Fig. 2. Fig. 3 shows the result that the gate voltage was fixed at the two points and the drain current was measured over a prolonged period of time with respect to each of the ON state and OFF state. It can be seen from Fig. 3 that the two states continue extremely stably.

[Example 2]

The materials used and the thicknesses thereof are as follows.

- 15 Semiconductor substrate 1: Si
- Insulator buffer layer 2:  $\text{HfO}_{2+u}$ ;  $u=0$ ; thickness of 10 nm
- Ferroelectric film 3:  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ; thickness of 400 nm
- 20 Gate electrode 4: Pt; thickness of 200 nm; gate length (length of distance from source region to drain region) of 10  $\mu\text{m}$
- Conductivity type of source region 5 and drain region 6: n-type
- 25 Conductivity type of region 7: p-type

HfO<sub>2+u</sub> (u=0) as an insulator buffer layer 2 was formed by pulsed-laser deposition. The laser used was a KrF excimer laser. The laser energy was 250 mJ per pulse, the pulse repetition frequency was 2 Hz, and the deposition time was 270 seconds. The temperature of the substrate was 200°C. The introduction gas was a nitrogen/oxygen mixed gas, in which the molar ratio N:O was 1:10<sup>-6</sup>. The pressure of this introduction gas in the deposition chamber was 0.1 Torr (13.33 Pa). SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> corresponding to a ferroelectric film 3 was also formed by pulsed-laser deposition. The kind and energy of the laser were the same as in the case of the insulator buffer layer 2 described above. The pulse repetition frequency was 5 Hz and the deposition time was 34 minutes. The temperature of the substrate was 400°C. The introduction gas was oxygen. The pressure of this introduction gas in the deposition chamber was 0.1 Torr (13.33 Pa). Platinum was formed as a gate electrode 4 by electron-beam vacuum deposition. After the formation of the gate electrode, a heat treatment was conducted at 800°C in oxygen atmospheric pressure for 1 hour in order to crystallize the SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>.

The results of experiments of the transistor produced in Example 2 above are then shown. Fig. 4 shows the results of a drain current I<sub>D</sub> when a gate voltage V<sub>G</sub> was applied to the gate electrode 4. The gate voltage was continuously changed from 8 V to -8 V and then changed from

-8 V to 8 V. The drain current changed as shown in Fig. 4 according to the specific properties of the ferroelectric. With the sweep of gate voltage, the drain current changed as shown by the arrows. The transistor can come into  
5 either of two states, i.e., an ON state and an OFF state, according to the direction of electric polarization memorized as represented by the two points shown in Fig. 4.

Fig. 5 shows the result that the gate voltage was fixed at the two points and the drain current was measured over a  
10 prolonged period of time with respect to each of the ON state and OFF state. It can be seen from Fig. 5 that the two states continue extremely stably.

In Fig. 2, the curve in the range of  $0 < V_G < 3$  V including the point shown by "ON STATE" and the curve in  
15 the range of  $1.6 \text{ V} < V_G < 4.6 \text{ V}$  including the point shown by "OFF STATE" have an almost parallel-shifting relationship with each other. The voltage corresponding to the width of this shifting is called memory window width. This memory window width gives one index to the memory  
20 characteristics of MFIS transistors. Too small values of the memory window width result in too small widths of set voltage, while too large values thereof result in an increased gate voltage for data writing. In Fig. 2, the gate voltage was changed over the range of  $\pm 6$  V. The  
25 memory window width when the width of the gate voltage

(sweep voltage) for Example 1 was changed is summarized in Fig. 6.

The source electrode, drain electrode, and substrate were made to have the same potential and the potential of the gate electrode was regulated so as to be higher than that by  $V_G$ . Under these conditions, the current  $I_G$  flowing through the insulator buffer layer and ferroelectric film arranged serially was measured. Fig. 7 shows the results of the measurement in Example 1.  $I_G$  corresponds to the leakage current in the insulator buffer layer and ferroelectric film arranged serially. When  $V_G \leq \pm 6$  V, then  $I_G$  is  $5 \times 10^{-10}$  A/cm<sup>2</sup> or lower. These values of leakage current are far lower than the values  $1 \times 10^{-8}$  A/cm<sup>2</sup> or lower for the same voltage range which are shown in Fig. 9 (b) at page 20 of non-patent document 2.

A test for determining the number of data rewriting operations was conducted. A voltage of +8 V was applied to the gate electrode for 500 ns to thereby form an ON state, and a voltage of -8 V was then applied for 500 ns to thereby form an OFF state. This operation as one cycle was repeated  $10^{12}$  times. Fig. 8 shows the test results for Example 1. It can be seen from Fig. 8 that even after the  $10^{12}$  repetitions (i.e.,  $2 \times 10^{12}$  data-rewriting operations), the ON-state drain current can be discriminated from the OFF-state drain current without any problem.

A test for determining dependence on writing pulse width was conducted. A single-pulse voltage having a pulse height of +8 V or -8 V was applied to the gate electrode to form an ON state or OFF state, while changing the width of the pulse. After this writing pulse application, a drain voltage of 0.1 V was applied to measure the drain current. The test results for Example 1 are shown in Fig. 9. It can be seen from Fig. 9 that even after the application of a pulse having a width of 500 ns, the ON-state drain current was higher than the OFF-state drain current by at least 4 digits.

A sample for Example 1 was analyzed for elemental composition by secondary ion mass spectrometry. The sample was dug from the back side of the silicon substrate in the order of silicon/insulator buffer layer/ferroelectric film, and each component was analyzed for elements. As a result, the insulator buffer layer was ascertained to contain nitrogen atoms as an additive. The amount thereof was  $2 \times 10^{21} \text{ cm}^{-3}$ . As stated above, the presence of these atoms not only serves to diminish structural defects in the insulator buffer layer to thereby reduce leakage current, but also serves to inhibit the formation of an oxide layer having a low-permittivity at the interface between the silicon and the insulator buffer layer.

In the case of Example 2 also, voltages were applied to the gate electrode in the same manner as that

shown in Fig. 7 and the resultant leakage current  $I_G$  was measured. The results of this test are shown in Fig. 10. In this Example also, the leakage current was lower than in the Example given in Fig. 9 (b) at page 20 of non-patent  
5 document 2.

A sample for Example 2 also was analyzed by secondary ion mass spectrometry. The method used was the same as in Example 1 described above. As a result, the insulator buffer layer was ascertained to contain nitrogen  
10 atoms as an additive. The amount thereof was  $2 \times 10^{20} \text{ cm}^{-3}$ . Same as in Example 1, the presence of these atoms serves to reduce leakage current and to inhibit the formation of an oxide layer having a low-permittivity at the interface between the silicon and the buffer layer.

15

[Examples 3 to 7 and Reference Example]

Transistors of Examples 3 to 7 were produced under completely the same conditions as in Example 1 and Example 2, except for the composition  $x$  in the insulator buffer  
20 layer. The values of  $x$  were:  $x=0.05$  in Example 3,  $x=0.12$  in Example 4,  $x=0.48$  in Example 5,  $x=0.68$  in Example 6, and  $x=0.85$  in Example 7. Furthermore, a transistor employing a material in which  $x=1$ , i.e.,  $\text{Al}_2\text{O}_3$ , as an insulator buffer layer was also produced as Reference Example. The gate  
25 voltage was swept and the drain current was measured to determine the memory window width of the MFIS transistor.



The sweep gate voltage was conducted under the same conditions of  $\pm 6$  V. The results thereof are shown in Fig. 11 together with the results in Example 1 and Example 2. The numerals in Fig. 11 correspond to the Example numbers.

5 R in Fig. 11 indicates Reference Example. When  $x$  is equal to 0 or is in the range of from above 0 to below 0.7, memory window widths of 1 V or larger were obtained. A gate voltage  $V_G$  of 7 V was applied to the transistor of Example 5 and the  $V_G$  was then returned to 0.95 V to form an  
10 ON state. This state in which  $V_G = 0.95$  V was maintained and the drain current in the ON state was measured as a function of time. Furthermore, a gate voltage  $V_G$  of -7 V was applied thereto and the  $V_G$  was then returned to 0.95 V to form an OFF state. This state in which  $V_G = 0.95$  V was  
15 maintained and the drain current in the OFF state was measured as a function of time. The results of those are shown in Fig. 12.

[Example 8]

20 A transistor of Example 8 was produced under completely the same conditions as in Example 1, except for the molar ratio of introduction oxygen gas to nitrogen gas. Namely, in this Example, the N:O in the introduction gas was 1:0.053. The gate voltage was swept and the drain  
25 current was measured to determine the memory window width of the MFIS transistor. The sweep gate voltage was

conducted under the same conditions of  $\pm 5$  V. The results thereof are shown in Fig. 13 together with the results in Example 1. The numerals in Fig. 13 correspond to the Example numbers.

5

[Example 9]

The materials used and the thicknesses thereof are as follows.

Semiconductor substrate 1: Si

10 Insulator buffer layer 2:  $\text{Hf}_{1-x}\text{Al}_{2x}\text{O}_{2+x+y}$ ;  $x=0.25$ ;  $y=0$ ;  
thickness of 10 nm

Ferroelectric film 3:  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ; thickness of 400  
nm

15 Gate electrode 4: Pt; thickness of 180 nm; gate  
length (length of distance from source region to drain  
region) of 10  $\mu\text{m}$

Conductivity type of source region 5 and drain  
region 6: n-type

Conductivity type of region 7: p-type

20 The silicon was subjected to a surface treatment in  
which the oxide layer remaining on the surface thereof was  
removed with buffered hydrofluoric acid, and a nitride film  
was thereafter formed with an rf plasma source. Namely,  
nitrogen gas was supplied at a rate of 1.5 cc/min to an rf  
25 plasma source attached to a vacuum vessel for pulsed-laser  
deposition and a nitrogen plasma was generated under the

conditions of an rf output of 200 W to form a silicon nitride film having a thickness of 1 nm on the silicon surface. The irradiation period with a nitrogen plasma beam was 10 minutes, and the temperature of the silicon substrate was 200°C during the irradiation period.

$\text{Hf}_{1-x}\text{Al}_{2x}\text{O}_{2+x+y}$  ( $x=0.25$ ;  $y=0$ ) as an insulator buffer layer 2 was formed by pulsed-laser deposition. The laser used was a KrF excimer laser. The laser energy was 250 mJ per pulse, the pulse repetition frequency was 2 Hz, and the deposition time was 270 seconds. The temperature of the substrate was 200°C. The introduction gas was nitrogen gas. The pressure of this introduction gas in the deposition chamber was 0.1 Torr (13.33 Pa).  $\text{SrBi}_2\text{Ta}_2\text{O}_9$

corresponding to a ferroelectric film 3 was also formed by pulsed-laser deposition. The kind and energy of the laser were the same as in the case of the insulator buffer layer 2 described above. The pulse repetition frequency was 5 Hz and the deposition time was 27 minutes. The temperature of the substrate was 400°C. The introduction gas was oxygen.

The pressure of this introduction gas in the deposition chamber was 0.1 Torr (13.33 Pa). Platinum was formed as a gate electrode 4 by electron-beam vacuum deposition. After the formation of the gate electrode, a heat treatment was conducted at 800°C in oxygen at atmospheric pressure for 1 hour in order to crystallize the  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ . A transistor was produced by using techniques for use in semiconductor

device production steps, such as photolithography and ion beam etching.

A gate voltage  $V_G$  of 8 V was applied to the transistor produced in Example 9, and the  $V_G$  was then  
5 returned to 0.2 V to form an ON state. This state in which  $V_G = 0.2$  V was maintained and the drain current in the ON state was measured as a function of time. Furthermore, a gate voltage  $V_G$  of -8 V was applied thereto and the  $V_G$  was then returned to 0.2 V to form an OFF state. This state in  
10 which  $V_G = 0.2$  V was maintained and the drain current in the OFF state was measured as a function of time. The results of those are shown in Fig. 14.

[Example 10]

15 The materials used and the thicknesses thereof are as follows.

Semiconductor substrate 1: Si

Insulator buffer layer 2:  $\text{Hf}_{1-x}\text{Al}_{2x}\text{O}_{2+x+y}$ ;  $x=0.25$ ;  $y=0$ ;  
thickness of 10 nm

20 Ferroelectric film 3:  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ; thickness of 400 nm

Gate electrode 4: Pt; thickness of 200 nm; gate length (length of distance from source region to drain region) of 10  $\mu\text{m}$

25 Conductivity type of source region 5 and drain region 6: n-type

Conductivity type of region 7: p-type

HfO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were separately prepared as target materials for pulsed-laser deposition to form Hf<sub>1-x</sub>Al<sub>2x</sub>O<sub>2+x+y</sub> (x=0.25; y=0) as an insulator buffer layer 2 by pulsed-laser deposition. The laser used was a KrF excimer laser. The laser energy was 250 mJ per pulse and the pulse repetition frequency was 2 Hz. HfO<sub>2</sub> was first deposited for 202 seconds and Al<sub>2</sub>O<sub>3</sub> was then deposited for 68 seconds. The temperature of the substrate was 200°C. The introduction gas was nitrogen gas. The pressure of this introduction gas in the deposition chamber was 0.1 Torr (13.33 Pa). SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> corresponding to a ferroelectric film 3 was also formed by pulsed-laser deposition. The kind and energy of the laser were the same as in the case of the insulator buffer layer 2 described above. The pulse repetition frequency was 5 Hz and the deposition time was 34 minutes. The temperature of the substrate was 400°C. The introduction gas was oxygen. The pressure of this introduction gas in the deposition chamber was 0.1 Torr (13.33 Pa). Platinum was formed as a gate electrode 4 by electron-beam vacuum deposition. After the formation of the gate electrode, a heat treatment was conducted at 800°C in oxygen at atmospheric pressure for 1 hour in order to crystallize the SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>. A transistor was produced by using techniques for use in semiconductor device production steps, such as photolithography and ion beam etching.

A gate voltage  $V_G$  of 6 V was applied to the transistor produced in Example 10, and the  $V_G$  was then returned to 0.9 V to form an ON state. This state in which  $V_G = 0.9$  V was maintained and the drain current in the ON state was measured as a function of time. Furthermore, a gate voltage  $V_G$  of -6 V was applied thereto and the  $V_G$  was then returned to 0.9 V to form an OFF state. This state in which  $V_G = 0.9$  V was maintained and the drain current in the OFF state was measured as a function of time. The results of those are shown in Fig. 15.